

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
6 January 2005 (06.01.2005)

PCT

(10) International Publication Number
WO 2005/000999 A1

(51) International Patent Classification⁷: **C10G 45/58**,
65/12

(21) International Application Number:
PCT/EP2004/051248

(22) International Filing Date: 25 June 2004 (25.06.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
03291598.5 27 June 2003 (27.06.2003) EP

(71) Applicant (for all designated States except US): **SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR
The Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **GERMAINE,
Gilbert, Robert, Bernard** [FR/FR]; 3, Route Departementale,
F-76650 Petit Couronne (FR). **STEENGE,
Wiecher, Derk, Evert** [NL/NL]; Badhuisweg 3, NL-1031
CM Amsterdam (NL).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance
Notes on Codes and Abbreviations" appearing at the beginning
of each regular issue of the PCT Gazette.



WO 2005/000999 A1

BEST AVAILABLE COPY

(54) Title: PROCESS TO PREPARE A LUBRICATING BASE OIL

(57) Abstract: Process to prepare a base oil having an paraffin content of between 75 and 95 wt% by subjecting a mixture of a Fischer-Tropsch derived feed and a petroleum derived feed to a catalytic pour point reducing treatment.

PROCESS TO PREPARE A LUBRICATING BASE OIL

The invention is directed to a process to prepare a base oil having an paraffin content of between 75 and 95 wt%.

5 WO-A-0246333 describes a process to prepare two viscosity grades of base oil by solvent dewaxing a fraction having a T95% point above 621 °C and catalytically dewaxing a fraction having a T95% point of below 621 °C. The two fractions are Fischer-Tropsch derived fractions. Optionally the heavier or the lower
10 boiling fraction may also be a slack wax, a distillate from crude oil, deasphalted residual stocks from crude oil.

NL-C-1015035 describes a process to prepare a base oil from a Fischer-Tropsch derived feed by performing a
15 hydroisomerisation step. The effluent of the hydroisomerisation step is distilled and a residue boiling above 380 °C is obtained. This residue is subjected to a catalytic dewaxing treatment using a catalyst containing platinum and ferrierite.

20 US-A-6294077 describes a catalytic dewaxing treatment wherein a catalyst is used consisting of ZSM-5 and platinum.

US-A-6025305 discloses a process wherein a Fischer-Tropsch wax feed is first hydroisomerised. The effluent
25 of the hydroisomerisation is then separated into fuels and lubricants. No pour point reducing treatment is disclosed in this publication.

US-A-2002/0146358 describes a process for hydroisomerisation of a Fischer-Tropsch derived wax feed.
30 The effluent of the hydroisomerisation step is distilled and a bottoms fraction comprising compounds having 20 or

- 2 -

more carbon atoms is obtained. This bottoms fraction may be subjected to a catalytic dewaxing treatment.

WO-A-0157166 describes the use of a highly paraffinic base oil as obtained from a Fischer-Tropsch wax in a motor engine lubricant formulation. The examples illustrate that such formulations will also consist of an ester, which according to the description of the patent are added to confer additional desired characteristics, such as additive solvency.

The use of ester co-base fluids in lubricant formulations as illustrated in WO-A-0157166 is not desired because such ester co-base fluids are not widely available and thus expensive. Additive solvency may be improved by using a paraffinic base stock, which contains less paraffins. Such base oils may be prepared by hydroisomerisation of petroleum derived waxes followed by a solvent or catalytic dewaxing step. A disadvantage of such a process is that the starting petroleum derived waxes, such as for example slack wax, are not easily obtainable. Furthermore such waxes may not always have the desired high paraffin content needed to make the desired base oils as per this invention.

The object of the present invention is to provide a process wherein a base oil with a paraffin content of between 75 and 95 wt% is obtained which does not have the disadvantages of the prior art processes.

This object is achieved by the following process. Process to prepare a base oil having an paraffin content of between 75 and 95 wt% by subjecting a mixture of a Fischer-Tropsch derived feed and a petroleum derived feed to a catalytic pour point reducing treatment.

Applicants found that by mixing a relatively small amount of a petroleum derived feed with a Fischer-Tropsch derived feed before performing a catalytic pour point

- 3 -

reducing treatment a base oil may be obtained having the desired properties.

5 The petroleum-derived fraction may in principle be any fraction boiling in the base oil range and containing non-paraffinic compounds. For this reason the wax content of such a feed will be typically low because wax typically consists for a greater part of normal paraffins. The wax content is suitably lower than 50 wt% and preferably lower than 30 wt%, as measured at -27 °C
10 using a 50/50 (vol/vol) methyl-ethyl ketone/toluene solvent mixture. In an even more preferred embodiment the wax content is very low and the feed is better described by its low pour point of below -10 °C and more preferably below -15 °C.

15 Preferably a petroleum-derived fraction is used which has been subjected to a hydroprocessing step in order to reduce aromatic, sulphur and nitrogen content of such fractions and improve some of the desired properties such as viscosity index. The hydroprocessing step may be a
20 hydrotreating optionally followed by a hydrocracking step. Such processes are for example performed when preparing base oils from a petroleum derived vacuum distillate or de-asphalted oils.

25 The petroleum derived feed preferably has an aromatic compound content of between 0 and 20 wt% and a naphthenic compound content of preferably between 15 and 90 wt%. These contents can be measured by well-known techniques such as the technique described at Example 3 of this specification.

30 A very interesting petroleum derived feed is the bottoms fraction of a fuels hydrocracker. With a fuels hydrocracker in the context of the present invention is meant a hydrocracker process which main products are naphtha, kerosene and gas oil. The conversion, expressed
35 in the weight percentage of the fraction in the feed to

- 4 -

the hydrotreater-hydrocracker which boils above 370 °C which are converted to products boiling below 370 °C, in the hydrotreater-hydrocracker process is typically above 50 wt%. Examples of possible fuels hydrocracker processes, which may yield a bottoms fraction which can be used in the present process, are described in the above referred to EP-A-699225, EP-A-649896, WO-A-9718278, EP-A-705321, EP-A-994173 and US-A-4851109.

Another interesting petroleum derived feed is the fraction obtained in a dedicated base oil hydrotreater-hydrocracker. In such a hydrotreater-hydrocracker the main products will boil in the base oil range. Typically such processes operate at a feed conversion of below 50 wt% and more typically between 20 and 40 wt%. The petroleum derived feed is thus the high boiling fraction as obtained in such a process prior to dewaxing.

Preferably the fuels hydrocracker is operated in two steps, consisting of a preliminary hydrotreating step followed by a hydrocracking step. In the hydrotreating step nitrogen and sulphur are removed and aromatics are saturated to naphthenes

An even more preferred feedstock is a dewaxed oil. This oil preferably has a pour point of below -10 °C, more preferably below -15 °C. Dewaxing can be solvent or catalytic dewaxing. The saturates content is preferably greater than 90 wt%, more preferably greater than 95 wt% and even more preferably greater than 98 wt% and most preferably higher than 99 wt%. The sulphur content is preferably less than 0.03 wt%, more preferably less than 0.01 wt% and even more preferably less than 0.001 wt%. An advantage of using a dewaxed oil having such low contents of sulphur, nitrogen and high contents of saturates is that no additional hydrofinishing is required after performing the pour point reducing step of the process of the present

- 5 -

invention. Advantageously the catalytic dewaxing will then not have to be performed at the higher pressure required for the subsequent hydrofinishing. In contrast it can be performed at a more preferred lower hydrogen pressure range of between 40 and 70 bars. Omitting such a hydrofinishing step is especially possible if the mineral derived dewaxed oils themselves are prepared by means of a process which does include a hydrofinishing step, preferably performed at a hydrogen pressure of above 100 bars. Examples of such hydrofinishing processes are for example those described below.

The oils are preferably made starting from a vacuum distillate or a de-asphalted vacuum residue of a mineral crude oil feedstock or from a waxy feed such as a slack wax, wherein the process includes a hydroprocessing step in which the sulphur and polar compounds are reduced to the preferred ranges. The viscosity index is preferably between 80-150, while good results have been achieved with oils having a viscosity index of between 80 and 120.

Preferably the T10wt% recovery point of this oil is between 200 and 450 °C, more preferably between 300 and 420 °C and the T90wt% recovery point is between 300 and 550 °C, more preferably between 400 and 550 °C. By using such a wide boiling oil it has been found possible to reduce the iso-paraffin content of the resultant base oils for both the lower viscosity grades, ranging from 2 cSt at 100 °C kinematic viscosity, to and including the higher viscosity grades having a kinematic viscosity at 100 °C of 15 cSt.

The dewaxed oil can be obtained as such by well known processes as for example described in Chapter 6 of Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker, Inc. New York, 1994, page 119-150. The preferred wide boiling oil can be prepared by mixing various viscosity grades of, preferably API Group II or

- 6 -

Group III, base oils. Examples of processes which yield an oil which can be used in this process are described in EP-A-0909304, EP-A-1137741, EP-A-1392799, EP-A-1311651. Examples of suitable dewaxed oils are for example Shell's
5 XHVI-4, XHVI-5.2 and XHVI-8 base oil products or ExxonMobil's Visom base oil grades and mixtures thereof. A possible commercial process which yields base oil for use in this invention is ExxonMobil's MSDWTM/MAXSATTM type of process which is said to yield a base oil
10 containing less than 1 wt% aromatics, < 1ppm sulphur, a Viscosity Index of greater than 120 and a pour point of less than -15 °C.

A more preferred dewaxed oil, which meets the above description, are those obtained when the bottoms fraction
15 of a fuels hydrocracker, as described above, is catalytically dewaxed followed by a hydrofinishing step. Examples of publications describing this route are WO-A-9802502, WO-A-0027950, WO-A-9500604, EP-A-0883664 and EP-A-0863963.

20 An additional advantage of adding a dewaxed oil as described above to the pour point reducing treatment of the process of the invention is that any undesired compounds in said oil, such as for example wax, polars, sulphur or nitrogen, can be further reduced in said
25 treatment. A further advantage is that the boiling range properties, pour point and/or the volatility of the final base oil can be controlled in a simple manner by control of the dewaxing conditions and the optional further distillation of the product obtained in said dewaxing
30 treatment. This is advantageous because it makes possible to use a wide variation of dewaxed oils in the process according to the invention. If for example such oils would have been blended after the dewaxing of a 100% Fischer-Tropsch derived feed and after a final
35 distillation much stringent property specifications, like

- 7 -

for example Noack volatility and viscosity, for the mineral derived blending component would have been required. Thus the process according to the invention makes it possible to use a wide variation of dewaxed oils having the above properties and obtain a base oil having the desired paraffin content and other desired base oil properties like especially Noack volatility and pour point.

The Fischer-Tropsch derived feed preferably is a hydroisomerized Fischer-Tropsch wax. Such a feed may be obtained by well-known processes, for example the so-called commercial Sasol process, the Shell Middle Distillate Process or by the non-commercial Exxon process. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US-A-4943672, US-A-5059299, WO-A-9934917 and WO-A-9920720. The process will generally comprise a Fischer-Tropsch synthesis and a hydroisomerisation step as described in these publications. Such a process to prepare the hydroisomerised Fischer-Tropsch feed for use as feed in the present process will comprise the following steps: (a) hydrocracking/hydroisomerising a Fischer-Tropsch product, (b) separating by means of distillation the product of step (a) into one or more gas oil fractions and a higher boiling Fischer-Tropsch derived feed according to this invention.

Preferably the Fischer-Tropsch product used as feed in step (a) is a product wherein the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms.

- 8 -

Applicants found that by performing the hydro-cracking/hydroisomerisation step with the relatively heavy feedstock a higher yield of gas oils as calculated on the feed to step (a) can be obtained. A further
5 advantage is that both fuels, for example gas oil, and the Fischer-Tropsch derived feed are prepared in one hydrocracking/hydroisomerisation process step. In a preferred embodiment of the present invention a fraction boiling above the Fischer-Tropsch derived feed is
10 isolated in step (b) and recycled to step (a).

A further advantage is that by performing step (a) on the relatively heavy feed a Fischer-Tropsch derived feed is prepared which already has a certain content of cyclo-paraffins.

15 The relatively heavy Fischer-Tropsch product used in step (a) has more preferably at least 50 wt%, and even more preferably at least 55 wt% of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon atoms and
20 compounds having at least 30 carbon atoms of the Fischer-Tropsch product is more preferably at least 0.4 and even more preferably at least 0.50. Preferably the Fischer-Tropsch product comprises a C_{20}^+ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor)
25 of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955.

The initial boiling point of the Fischer-Tropsch product may range up to 400 °C, but is preferably
30 below 200 °C. Preferably any compounds having 4 or less carbon atoms and any compounds having a boiling point in that range are separated from a Fischer-Tropsch synthesis product before the Fischer-Tropsch synthesis product is used in step (a). The Fischer-Tropsch product as
35 described in detail above is a Fischer-Tropsch product,

- 9 -

which has not been subjected to a hydroconversion step as defined according to the present invention. The content of non-branched compounds in the Fischer-Tropsch product will therefore be above 80 wt%. In addition to the Fischer-Tropsch product also other fractions may be additionally processed in step (a). Possible other fractions may suitably be the optional higher boiling fraction obtained in step (b) or part of said fraction and/or off-spec base oil fractions as obtained in the pour point reducing treatment of the process of the present invention.

Such a Fischer-Tropsch product can be obtained by any process, which yields a relatively heavy Fischer-Tropsch product as described above. Not all Fischer-Tropsch processes yield such a heavy product. An example of a suitable Fischer-Tropsch process is described in WO-A-9934917 and in AU-A-698392. These processes may yields a Fischer-Tropsch product as described above.

The Fischer-Tropsch product will contain no or very little sulphur and nitrogen containing compounds. This is typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no impurities. Sulphur and nitrogen levels will generally be below the detection limits, which are currently 2 ppm for sulphur and 1 ppm for nitrogen respectively.

The Fischer-Tropsch product may optionally be subjected to a mild hydrotreatment step in order to remove any oxygenates and saturate any olefinic compounds present in the reaction product of the Fischer-Tropsch reaction. Such a hydrotreatment is described in EP-B-668342. The mildness of the hydrotreating step is preferably expressed in that the degree of conversion in this step is less than 20 wt% and more preferably less than 10 wt%. The conversion is here defined as the weight percentage of the feed boiling above 370 °C, which reacts

- 10 -

to a fraction boiling below 370 °C. After such a mild hydrotreatment lower boiling compounds, having four or less carbon atoms and other compounds boiling in that range, will preferably be removed from the effluent before it is used in step (a).

The hydrocracking/hydroisomerisation reaction of step (a) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being suitable for this reaction of which some will be described in more detail below. The catalyst may in principle be any catalyst known in the art to be suitable for isomerising paraffinic molecules. In general, suitable hydroconversion catalysts are those comprising a hydrogenation component supported on a refractory oxide carrier, such as amorphous silica-alumina, alumina, fluorided alumina, molecular sieves (zeolites) or mixtures of two or more of these. One type of preferred catalysts to be applied in the hydroconversion step in accordance with the present invention are hydroconversion catalysts comprising platinum and/or palladium as the hydrogenation component. A very much preferred hydroconversion catalyst comprises platinum and palladium supported on an amorphous silica-alumina (ASA) carrier. The platinum and/or palladium is suitably present in an amount of from 0.1 to 5.0% by weight, more suitably from 0.2 to 2.0% by weight, calculated as element and based on total weight of carrier. If both present, the weight ratio of platinum to palladium (calculated as element) may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5. Examples of suitable noble metal on ASA catalysts are, for instance, disclosed in WO-A-9410264 and EP-A-0582347. Other suitable noble metal-based catalysts, such as platinum on a fluorided alumina carrier, are disclosed in

- 11 -

e.g. US-A-5059299 and WO-A-9220759. Preferably such catalysts do not comprise a molecular sieve, more preferably such catalysts do not comprise zeolite beta.

5 A second type of suitable hydroconversion catalysts are those comprising at least one Group VIB metal, preferably tungsten and/or molybdenum, and at least one non-noble Group VIII metal, preferably nickel and/or cobalt, as the hydrogenation component. Usually both
10 metals are present as oxides, sulphides or a combination thereof. The Group VIB metal is suitably present in an amount of from 1 to 35% by weight, more suitably from 5 to 30% by weight, calculated as element and based on total weight of catalyst. The non-noble Group VIII
15 metal is suitably present in an amount of from 1 to 25 %wt, preferably 2 to 15 %wt, calculated as element and based on total weight of carrier. A hydroconversion catalyst of this type which has been found particularly suitable is a catalyst comprising nickel and tungsten supported on fluorided alumina.

20 A preferred catalyst which can be used in a non-sulphided form comprises a non-noble Group VIII metal, e.g., iron, nickel, in conjunction with a Group IB metal, e.g., copper, supported on an acidic support. The catalyst has a surface area in the range
25 of 200-500 m²/gm, preferably 0.35 to 0.80 ml/gm, as determined by water adsorption, and a bulk density of about 0.5-1.0 g/ml. The catalyst support is preferably an amorphous silica-alumina where the alumina is present in amounts of less than about 30 wt%, preferably 5-30 wt%,
30 more preferably 10-20 wt%. Also, the support may contain small amounts, e.g., 20-30 wt%, of a binder, e.g., alumina, silica, Group IVA metal oxides, and various types of clays, magnesia, etc., preferably alumina.

- 12 -

The preparation of amorphous silica-alumina microspheres has been described in Ryland, Lloyd B., Tamele, M.W., and Wilson, J.N., Cracking Catalysts, Catalysis: volume VII, Ed. Paul H. Emmett, Reinhold
5 Publishing Corporation, New York, 1960, pp. 5-9.

The catalyst is prepared by co-impregnating the metals from solutions onto the support, drying at 100-150 °C, and calcining in air at 200-550 °C. The
10 Group VIII metal is present in amounts of about 15 wt% or less, preferably 1-12 wt%, while the Group IB metal is usually present in lesser amounts, e.g., 1:2 to about 1:20 weight ratio respecting the Group VIII metal.

A typical catalyst is shown below:

	Ni, wt%	2.5-3.5
15	Cu, wt%	0.25-0.35
	Al ₂ O ₃ -SiO ₂ wt%	65- 75
	Al ₂ O ₃ (binder) wt%	25-30
	Surface Area	290-325 m ² /gm
	Pore Volume (Hg)	0.35-0.45 ml/gm
20	Bulk Density	0.58-0.68 g/ml

Another class of suitable hydroconversion catalysts are those based on zeolitic materials, suitably comprising at least one Group VIII metal component, preferably Pt and/or Pd, as the hydrogenation component.
25 Suitable zeolitic materials, then, include Zeolite beta, Zeolite Y, Ultra Stable Y, ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-35, SSZ-32, ferrierite, zeolite beta, mordenite and silica-aluminophosphates, such as SAPO-11 and SAPO-31.

- 13 -

Examples of suitable hydroisomerisation catalysts are, for instance, described in WO-A-9201657.

5 In step (a) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range of from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be
10 supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower
15 than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

The conversion in step (a) as defined as the weight percentage of the feed boiling above 370 °C which reacts
20 per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not more than 80 wt%, more preferably not more than 70 wt%. The feed as used above in the definition is the total hydrocarbon feed fed to step (a), thus also any
25 optional recycle of the higher boiling fraction as obtained in step (b).

In step (b) the product of step (a) is separated into one or more gas oil fractions and a Fischer-Tropsch derived feed having preferably a T10 wt% boiling point of
30 between 200 and 450 °C. If a higher boiling fraction is separated from the Fischer Tropsch feed the T90 wt% of said feed is preferably between 300 °C, and preferably between 430 and 550 °C. The separation is preferably performed by means of a first distillation at about
35 atmospheric conditions, preferably at a pressure of

- 14 -

between 1.2-2 bara, wherein the gas oil product and lower boiling fractions, such as naphtha and kerosine fractions, are separated from the higher boiling fraction of the product of step (a). The higher boiling fraction, of which suitably at least 95 wt% boils above 370 °C, may be further separated in a vacuum distillation step wherein a higher boiling fraction is separated. The vacuum distillation is suitably performed at a pressure of between 0.001 and 0.05 bara.

The vacuum distillation of step (b) is preferably operated such that the desired Fischer Tropsch derived feed is obtained boiling in the specified range and having a kinematic viscosity, which relates to the base oil end product(s) specification. The kinematic viscosity at 100 °C of the Fischer Tropsch derived feed is preferably between 3 and 10 cSt.

The mixture of petroleum derived and Fischer-Tropsch derived feeds will suitably have a viscosity corresponding to the desired viscosity of the base oil product. Preferably the kinematic viscosity at 100 °C of the mixture is between 3 and 10 cSt. Suitable distillate fractions have a T10wt% boiling point of between 200 and 450 °C, preferably between 300 and 420 °C and a T90wt% boiling point of between 300 and 550 °C, preferably between 400 and 550 °C. The fraction of petroleum derived feed in the mixture is preferably higher than 5 wt%, more preferably higher than 10 wt% and preferably lower than 50 wt% and more preferably below 30 wt% and even more preferably below 25 wt%. The actual content of petroleum-derived feed in the mixture will of course depend on the paraffin content of said feed. The mixture will preferably contain less than 50 ppm sulphur and/or less than 10 ppm nitrogen.

With the catalytic pour point reducing treatment is understood every process wherein the pour point of the

- 15 -

base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C.

5 The catalytic dewaxing or pour point reducing process can be performed by any process wherein in the presence of a catalyst and hydrogen the pour point of the mixture is reduced as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the distillate base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminophosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

30 The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The

- 16 -

binder is preferably a porous binder material, for example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania
5 as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a low acidity refractory oxide binder material which is essentially free of alumina is used. Examples of these
10 binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most preferred binder is silica.

A preferred class of dewaxing catalysts comprise
15 intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate
20 zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or WO-A-2000029511.
25 Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22 as for example described in WO-A-200029511 and
30 EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar,
35 preferably from 40 to 70 bar, weight hourly space

- 17 -

velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil. By varying the temperature between 315 and 375 °C at a pressure of between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having different pour point specifications varying from suitably lower than -60 to -10 °C.

Optionally a noble metal guard bed may be positioned just upstream the dewaxing step, for example as a separate catalyst bed in the dewaxing reactor. Such a guard bed is advantageous to remove any remaining sulphur and especially nitrogen compounds present in the feed to the dewaxing process of the present invention. Such a guard bed is suitably used when a bottoms fraction of a fuels hydrocracker process is used as the petroleum derived feed. An example of such a process is described in WO-A-9802503, which reference is hereby incorporated by reference.

After performing the pour point reducing treatment lower boiling compounds formed during said treatment are suitably removed, preferably by means of distillation, optionally in combination with an initial flashing step.

The effluent of the pour point reducing treatment may suitably be subjected to a hydrogenation treatment. Hydrogenation may be performed on the entire effluent or on specific base oil grades after the above described fractionation. This may be required in order to reduce the content of aromatic compounds in the reduced pour point product to preferably values of below 1 wt%. Such a hydrogenation is also referred to as a hydrofinishing step. This step is suitably carried out at a temperature between 180 and 380 °C, a total pressure of

- 18 -

between 10 to 250 bar and preferably above 100 bar and more preferably between 120 and 250 bar. The WHSV (Weight hourly space velocity) ranges from 0.3 to 2 kg of oil per litre of catalyst per hour (kg/l.h). Preferably a
5 hydrogenation is performed in the same reactor as the catalytic dewaxing reactor. In such a reactor the beds of dewaxing catalyst and hydrogenation catalyst will be placed in a stacked bed on top of each other.

The hydrogenation catalyst is suitably a supported
10 catalyst comprising a dispersed Group VIII metal. Possible Group VIII metals are cobalt, nickel, palladium and platinum. Cobalt and nickel containing catalysts may also comprise a Group VIB metal, suitably molybdenum and tungsten. Suitable carrier or support materials are low
15 acidity amorphous refractory oxides. Examples of suitable amorphous refractory oxides include inorganic oxides, such as alumina, silica, titania, zirconia, boria, silica-alumina, fluorided alumina, fluorided silica-alumina and mixtures of two or more of these.

20 Examples of suitable hydrogenation catalysts are nickel-molybdenum containing catalyst such as KF-847 and KF-8010 (AKZO Nobel) M-8-24 and M-8-25 (BASF), and C-424, DN-190, HDS-3 and HDS-4 (Criterion); nickel-tungsten containing catalysts such as NI-4342 and NI-4352
25 (Engelhard) and C-454 (Criterion); cobalt-molybdenum containing catalysts such as KF-330 (AKZO-Nobel), HDS-22 (Criterion) and HPC-601 (Engelhard). Preferably platinum containing and more preferably platinum and palladium containing catalysts are used. Preferred supports for
30 these palladium and/or platinum containing catalysts are amorphous silica-alumina. Examples of suitable silica-alumina carriers are disclosed in WO-A-9410263. A preferred catalyst comprises an alloy of palladium and platinum preferably supported on an amorphous silica-
35 alumina carrier of which the commercially available

- 19 -

catalyst C-624 of Criterion Catalyst Company (Houston, TX) is an example.

After performing the catalytic pour point reducing treatment or after the optional hydrofinishing step

5 hydrogen is suitably separated from the dewaxed/hydrofinished effluent, contacted with a means to remove hydrogen sulphide and recycled to said catalytic pour point reducing treatment. Such means could be amine washing of the hydrogen recycle stream. If the content of

10 hydrogen sulphide is expected to be low, for example below 100 ppm or even below 20 ppm, in the recycle stream contacting said stream with a suitable adsorbent will be preferred. Examples of suitable heterogeneous adsorbents are comprise at least one metal or oxide of the metal,

15 the metal(s) being selected from Fe, Ni, Co, Ag, Sn Re, Mo, Cu, Pt, Pd and Zn. In a preferred embodiment, the metal is at least one of Fe, Ni, Co, Cu, and Zn. In a more preferred embodiment the adsorbent is zinc oxide. The adsorbent may be supported on an inorganic support

20 material in order to, for example, increase surface area, pore volume, and pore diameter. Suitable support materials contain at least one inorganic refractory support materials including, but not necessarily limited to, alumina, silica, zirconia, carbon, silicon carbide,

25 kieselguhr, amorphous and crystalline silica-aluminas, silica-magnesias, aluminophosphates, boria, titania, and zinc oxide. Preferred support materials include alumina, zirconia, and silica. The metal(s) or metal oxide(s) may be loaded onto these supports by conventional techniques

30 known in the art. Non-limiting examples of suitable supported metal and metal oxide based regenerable sulfur adsorbents include, but are not necessarily limited to: Co/Al₂O₃; Co/SiO₂; Co/TiO₂; Co/ZrO₂; Ni/Al₂O₃; Ni/SiO₂; Ni/ZrO₂; Cu/Al₂O₃; Cu/SiO₂; Cu/ZrO₂; Fe/Al₂O₃; Fe/SiO₂;

35 Fe/ZrO₂; Co/Cu/Al₂O₃; Co/Cu/SiO₂; Ni/Cu/SiO₂; Ni/Cu/ZrO₂;

- 20 -

Co/Pt/Al₂O₃; Co/Pd/SiO₂; Co/Sn/Al₂O₃; Ni/Sn/SiO₂;
Zn/Al₂O₃, ZnO/SiO₂, Co/ZnO; Mo/ZnO; Ni/ZnO; Co/Mo/ZnO;
Ni/Mo/ZnO; Pt/ZnO; Pd/ZnO; Pt/Pd/ZnO. The adsorbent may
also be employed as a bulk metal oxide or as a bulk
5 metal, including but not necessarily limited to, a finely
divided skeleton metal, including Raney metals, ponderous
metals, Rieke metals, and metal sponges. The temperature
and pressure conditions during said contacting are
preferably within the ranges specified for the catalytic
10 pour point reduction.

From the effluent of the pour point reducing
treatment and the optional hydrogenation treatment one or
more base oil grades may be isolated by means of
fractionation. Base oil products having kinematic
15 viscosity at 100 °C of between 2 and 10 cSt, having a
volatility of between 8 and 11% (according to CEC
L40 T87) and a pour point of between -20 and -60 °C
(according to ASTM D 97) may advantageously be obtained.

The content of paraffins is more preferably less
20 than 90 wt% and more preferably higher than 80 wt%.

The above-described base oil can suitably find
use as base oil for an Automatic Transmission Fluids
(ATF), motor engine oils, electrical oils or
transformer oils and refrigerator oils. lubricant
25 formulations such as motor engine oils of the 0W-x
and 5W-x specification according to the SAE J-300
viscosity classification, wherein x is 20, 30, 40, 50
or 60 may be advantageously made using this base oil.

It has been found that lubricant formulations can be
30 prepared with the base oils obtainable by the process of
the current invention without the need to add high
contents of additional ester or aromatic co-base oils.
Preferably less than 15 wt% and more preferably less
than 10 wt% of such ester or aromatic co-base oil is
35 present in such formulations.

- 21 -

The Fischer-Tropsch process is sometimes performed at a remote location far away from the end-users of the base oils. It has also been found that for certain applications the end-users do not necessarily require
5 base oils having the high paraffin contents as prepared by the prior art processes which operate on 100 % Fischer-Tropsch derived feed. For these applications blending with mineral derived base oils containing less paraffins will have to take place such to reduce the
10 paraffin content. It is however not always the case that suitable mineral blending components are found near the end users. As explained above such blending components need to have the right volatility and viscosity to obtain the desired blend. The present invention solves this
15 problem, wherein at the remote location the desired lower paraffin base oils are prepared having the specified volatility and viscosity and in addition pour point and viscosity index from a petroleum derived feed which does not have to meet all the stringent quality properties.
20 Thus a process is obtained wherein for example the petroleum derived feed is obtained from one location and the base oils obtained by the present process are marketed in many different locations. In a preferred embodiment the petroleum derived feed is shipped to the
25 remote location from another location and part of the base oils as made by the present process are shipped to said other location making use of the same vessel. This is advantageous because efficient use of shipping capacity between the two locations is thus achieved. Such
30 a method is especially suitable when the petroleum derived feed is a dewaxed oil having the preferred low sulphur contents as described above.

- 22 -

Example 1 and 2

A blend of 20 wt% of a bottoms fraction of a fuels hydrocracker and 80 wt% of a Fischer-Tropsch derived Waxy Raffinate as obtained from Shell MDS (Malaysia) Sdn Bhd (marketed as Shell MDS Waxy Raffinate) was prepared. The Shell MDS Waxy Raffinate is a partly isomerised Fischer-Tropsch derived fraction.

The above blend was contacted with a dewaxing catalyst consisting of 0.7 wt% platinum, 25 wt% ZSM-12 and a silica binder. The dewaxing conditions were 40 bar hydrogen, WHSV = 1 kg/l.h, and a hydrogen gas rate of 700 Nl/kg feed. The experiment was carried out at two different reaction temperatures, namely 304 °C (Example 1) and 297 °C (Example 2).

From the effluent of the dewaxing step a base oil boiling between 400 and 460 °C was isolated from lower and higher boiling products. This fraction was analysed. The yield and properties of this fraction having a kinematic viscosity of about 4 cSt are reported in Table 2. Table 5 lists the composition of these base oils.

Table 1

Feed	bottoms fraction of a fuels hydrocracker	Shell MDS Waxy Raffinate
Density (D70/4)	0.8036	0.7845
Pour point °C	+39	+42 °C
Nitrogen (ppmw)	< 1	n.a. (*)
Sulphur (ppmw)	< 2	n.a. (*)

- 23 -

Kinematic viscosity at 100 °C cSt	4.439	5.062
Initial boiling point (IBP) °C	269	361
IBP-390 °C (wt%)	26.9	4.4
390-520 °C (wt%)	63.0	84.8
520 °C - FBP (wt%)	10.1	10.8
Final boiling point (FBP) °C	602	587
Wax content (wt%)	17.8	16.4

* N.a.= not analysed. In view of Fischer-Tropsch source it is expected that these values are lower than the detection limit

5 Table 1a

Composition of the bottoms fraction of a fuels hydrocracker used in Examples 1 and 2	Mass %
Paraffinic compounds	68%
Naphthenic compounds	29%
Aromatic compounds	3 %

- 24 -

Comparative Experiment A and B

Example 1 was repeated with a 100% pure Fischer-Tropsch Waxy Raffinate feed of Table 1. The reactor temperature was varied to obtain a total liquid product (i.e. the total liquid effluent of the dewaxing step) having a pour point as in Example 1 or close to said pour point. See Table 2 for results and table 5 for composition.

10

Table 2

Example	1	A	2	B
Feed	20/80 blend	Fischer-Tropsch WR	20/80 blend	Fischer-Tropsch WR
Reactor temperature (°C)	304	315	297	307
Yield Base oil between 400 and 460 °C on feed (wt%)	43.2	37.3	45.2	34.9
Base oil pour point (°C)	-31	-35	-17	-19
Kinematic viscosity at 100 °C of base oil (cSt)	4.15	4.022	4.109	3.879
Viscosity Index of base oil	129	130	132	133

- 26 -

Example 3

12.7 weight parts of a wide boiling dewaxed and hydrofinished oil having the properties as listed in Table 3 was mixed with 87.3 weight parts of a Shell MDS waxy Raffinate having the properties listed in Table 3. The wide boiling dewaxed and hydrofinished oil was prepared by catalytic dewaxing of a bottoms fraction of a fuels hydrocracker followed by a hydrofinishing step on the dewaxed effluent. The hydrocracker in turn was fed by a vacuum distillate of a mineral crude feed.

This blend of API Group II base oils was mixed with a Shell MDS waxy Raffinate having the properties listed in Table 3.

Table 3

Feed	Wide boiling Mineral dewaxed and hydrofinished Oil	Shell MDS Waxy Raffinate
Density (D20/4)	0.847	0.784
Pour point (°C)	-24	45
Nitrogen (ppmw)	< 1	< 1
Sulphur (ppmw)	8	< 2
Kinematic viscosity at 100 °C	4.679	5.098

- 27 -

boiling point (IBP) °C		
IBP-390 °C (wt%)	20.6	2.3
390-520 °C (wt%)	67.9	88.4
520 °C - FBP (wt%)	11.5	9.3
Final boiling point (FBP) °C	600	573
Wax content (wt%)	No wax	27.1

5 The above blend was contacted with a dewaxing catalyst consisting of 0.7 wt% platinum, 25 wt% ZSM-12 and a silica binder. The dewaxing conditions were 40 bar hydrogen, WHSV = 1 kg/l.h, and a hydrogen gas rate of 700 Nl/kg feed. The experiment was carried out at two different reaction temperatures, namely 317 °C.

10 From the effluent of the dewaxing step a base oil boiling between 400 and 470 °C was isolated from lower and higher boiling products. The yield of this fraction was 40 wt% on the blended feed. The pour point was -30 °C, the Kinematic viscosity at 100 °C was 4,059 cSt and the Viscosity Index was 129. The composition of this
15 fraction was analysed using the following technique.

The cyclo-paraffin (naphthenic compounds) content in this mixture of cyclo-, normal and iso-paraffins is

- 28 -

measured by the following method. Any other method
resulting in the same results may also be used. The base
oil sample is first separated into a polar (aromatic)
phase and a non-polar (saturates) phase by making use of
5 a high performance liquid chromatography (HPLC) method
IP368/01, wherein as mobile phase pentane is used instead
of hexane as the method states. The saturates and
aromatic fractions are then analyzed using a Finnigan
MAT90 mass spectrometer equipped with a Field
10 desorption/Field Ionisation (FD/FI) interface, wherein FI
(a "soft" ionisation technique) is used for the
quantitative determination of hydrocarbon types in terms
of carbon number and hydrogen deficiency of this
particular base oil fraction. The instrument conditions
15 to achieve such a soft ionization technique are a source
temperature of 30 °C, an extraction voltage of 5kV, an
emitter current of 5mA and a probe temperature ramp of
40°C to 400°C (20°C/min)

The type classification of compounds in mass
20 spectrometry is determined by the characteristic ions
formed and is normally classified by "z number". This is
given by the general formula for all hydrocarbon species:
 C_nH_{2n+z} . Because the saturates phase is analysed
separately from the aromatic phase it is possible to
25 determine the content of the different (cyclo)-paraffins
having the same stoichiometry. The results of the mass
spectrometer are processed using commercial software
(poly 32; available from Sierra Analytics LLC, 3453
Dragoo Park Drive, Modesto, Calif. GA95350 USA) to
30 determine the relative proportions of each hydrocarbon
type and the average molecular weight and polydispersity
of the saturates and aromatics fractions.

- 29 -

For the base oil fraction boiling between 400 and 470 °C as obtained above the composition as listed in Table 5 was determined using the above technique.

Table 5

Composition as determined by method example 3	Base Oil of Example 1	Base Oil of Example 2	Base oil of Example 3	Base oil of Experiment A	Base oil of Experiment B
Iso- and normal paraffins (wt%)	74%	82%	83	86%	88%
Naphthenic compounds (wt%)	25%	17%	16%	13%	11%
Polars (wt%)	1%	1%	1%	1%	1%

- 31 -

C L A I M S

1. Process to prepare a base oil having an paraffin content of between 75 and 95 wt% by subjecting a mixture of a Fischer-Tropsch derived feed and a petroleum derived feed to a catalytic pour point reducing treatment.
- 5 2. Process according to claim 1, wherein the petroleum derived feed is a bottoms fraction of a fuels hydrocracker.
3. Process according to claim 2, wherein the content of sulphur in the mixed feed to the pour point reducing treatment is below 50 ppm and the content of nitrogen in
10 the mixed feed to the pour point reducing treatment is below 10 ppm.
4. Process according to any one of claims 1-3, wherein the wax content in the petroleum derived feed is below
15 50wt%, preferably below 30 wt%.
5. Process according to claim 4, wherein the pour point of the petroleum derived feed is below -10 °C.
6. Process according to any one of claims 1-5, wherein the petroleum derived feed has an aromatic content of
20 between 0 and 20 wt% and a naphthenic compound content of preferably between 15 and 90 wt%.
7. Process according to claim 6, wherein the petroleum derived feed has a saturates content of greater than 98 wt% a viscosity index of between 80 and 150 and a sulphur
25 content of below 0.001 wt%.
8. Process according to claim 7, wherein the petroleum derived feed has been obtained in a process involving a hydrofinishing step performed at a hydrogen pressure of greater than 100 bars.

- 32 -

9. Process according to any one of claims 1-8, wherein the fraction of petroleum derived feed in the mixture is higher than 5 wt% and lower than 50 wt%.
10. Process according to any one of claims 1-9, wherein
5 the base oil is hydrogenated after performing the pour point reducing treatment such that the content of aromatics is below 1 wt%.
11. Process according to any one of claims 1-10, wherein
10 the catalytic pour point reducing treatment is a catalytic dewaxing process performed in the presence of a catalyst comprising a Group VIII metal and an intermediate pore size zeolite having pore diameter between 0.35 and 0.8 nm, and a binder.
12. Process according to any one of claims 1-11, wherein
15 after performing the catalytic pour point reducing treatment hydrogen is separated from the dewaxed effluent, contacted with a heterogeneous adsorbent selective for removing hydrogen sulphide and recycled to said catalytic pour point reducing treatment.
13. Process according to claim 12, wherein the
20 heterogeneous adsorbent is zinc oxide.
14. Process according to any one of claims 1-13, wherein the Fischer-Tropsch feed is obtained by hydroisomerisation of a Fischer-Tropsch product.
15. Process according to claim 14, wherein the
25 hydroisomerised Fischer-Tropsch feed is obtained by means of the following steps:
(a) hydrocracking/hydroisomerising a Fischer-Tropsch product,
30 (b) separating by means of distillation the product of step (a) into one or more gas oil fractions and a higher boiling Fischer-Tropsch derived feed.
16. Process according to claim 15, wherein the Fischer-Tropsch product used as feed in step (a) is a product
35 wherein the weight ratio of compounds having at least 60

- 33 -

or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.4 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/051248

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G45/58 C10G65/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 294 077 B1 (DOUGHERTY RICHARD C ET AL) 25 September 2001 (2001-09-25) column 5, line 18 - line 36 column 7, line 53 - column 9, line 39; claims 1,2; examples 3,4; table 3	1-16
X	WO 02/46333 A (CHEVRON USA INC) 13 June 2002 (2002-06-13) page 6, line 1 - line 11 page 17, line 3 - line 6; claims 1,8 page 10, line 24 - page 13, line 27 page 7, line 15 - line 24 -/-	1-16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

13 October 2004

Date of mailing of the international search report

20/10/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Deurinck, P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/051248

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NL 1 015 035 C (INST FRANCAIS DU PETROL) 12 February 2001 (2001-02-12) page 17, line 9 - line 19 page 30; claims 1,16,17,26 page 20, line 1 - page 21, line 24 page 18, line 16 - line 26 -----	1-16
X	US 6 025 305 A (ALDRICH HAVEN SCOTT ET AL) 15 February 2000 (2000-02-15) column 3, line 1 - column 4, line 65 column 5, line 10 - line 18; claims 1,4 -----	1-16
X	US 2002/146358 A1 (SMITH BEN D ET AL) 10 October 2002 (2002-10-10) paragraphs '0020! - '0022!, '0050!, '0085!, '0087!, '0096!, '0097!; claims 1,2,5,11 -----	1-16
A	US 2003/088133 A1 (O'REAR DENNIS J) 8 May 2003 (2003-05-08) paragraph '0078! - paragraph '0114!; claims 1,7 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/051248

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 6294077	B1	25-09-2001	AU	767436 B2	13-11-2003
			AU	3325501 A	14-08-2001
			CA	2399616 A1	09-08-2001
			EP	1259578 A1	27-11-2002
			JP	2003522251 T	22-07-2003
			WO	0157159 A1	09-08-2001
WO 0246333	A	13-06-2002	US	6773578 B1	10-08-2004
			AU	3768602 A	18-06-2002
			AU	9343601 A	06-06-2002
			BR	0115367 A	06-01-2004
			GB	2374348 A ,B	16-10-2002
			GB	2386608 A ,B	24-09-2003
			JP	2004515601 T	27-05-2004
			NL	1019472 C2	07-08-2002
			NL	1019472 A1	06-06-2002
			WO	0246333 A2	13-06-2002
			ZA	200109932 A	27-06-2002
NL 1015035	C	12-02-2001	FR	2805542 A1	31-08-2001
			FR	2792946 A1	03-11-2000
			ES	2190303 A1	16-07-2003
			JP	2000345171 A	12-12-2000
			NL	1015035 C2	12-02-2001
			NL	1015035 A1	31-10-2000
			US	6602402 B1	05-08-2003
US 6025305	A	15-02-2000	CA	2337888 A1	17-02-2000
			DE	69918443 D1	05-08-2004
			EP	1102828 A1	30-05-2001
			JP	2003517496 T	27-05-2003
			WO	0008116 A1	17-02-2000
US 2002146358	A1	10-10-2002	AU	2768502 A	10-10-2002
			BR	0208326 A	09-03-2004
			GB	2381002 A ,B	23-04-2003
			JP	2004526034 T	26-08-2004
			NL	1020311 C2	07-10-2002
			WO	02081598 A1	17-10-2002
			ZA	200202596 A	24-10-2002
US 2003088133	A1	08-05-2003	GB	2384246 A	23-07-2003
			NL	1021691 C2	11-03-2004
			NL	1021691 A1	23-04-2003
			WO	03035585 A1	01-05-2003
			US	2004053796 A1	18-03-2004
			ZA	200208263 A	14-05-2003

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)